Filtration Assisted Crystallization Technology: Heterogeneous seeds enable fast crystallization and easy filtration

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Abstract

FACT, which stands for Filtration Assisted Crystallization Technology, is a hybrid process based on heterogeneous crystallization and filtration. During the process development heterogeneous seeds are selected, which enable a combination of fast crystallization and easy filtration. Water softening is chosen to illustrate the principle and potential of FACT, but the FACT process can also be applied for the removal of heavy metals, phosphate and fluoride from process/waste water streams or the change of the shape and/or size of crystals/particles.
Water softening is often applied in order to prevent scaling in heat exchangers. In the FACT-concept softening is achieved by the precipitation of calcium carbonate ($CaCO_3$) on the surface of a small amount of heterogeneous seeds in a crystallizer. Next, a filter separates the softened water from the grown seeds, which are recycled to the crystallizer as a concentrated suspension. The heterogeneous seeds grow during the softening process and are bled off intermittently when they reached the required size. FACT is compact due to the fast crystallization and easy filtration and it can compete technically and economically with alternative softening technologies like the pellet reactor and ion exchange.
The paper presents the results for the selection of heterogeneous seeds. The softening of ground water and a process water stream from a paper mill was investigated with a FACT pilot plant. The pilot plant results of the FACT process are compared technically and economically with other softening technique based on heterogeneous crystallization.

1. Introduction

Hard water can easily cause scaling in heat exchangers, which reduces heat transfer and increases costs for maintenance costs. Therefore, softening techniques like the pellet reactor, ion exchange and nanofiltration, are often used to remove hardness before the water is heated. This contribution presents FACT, a new generic process that amongst others can be applied for the removal of hardness by means of the precipitation of calcium carbonate ($CaCO_3$) on heterogeneous seeds. During the development of a FACT application heterogeneous seeds are selected which accelerate the crystallization and which can easily be separated from the treated liquid. The acceleration of the crystallization is caused by stimulation of the heterogeneous nucleation. Examples of interactions between the seed and the material to be crystallized that can stimulate heterogeneous nucleation are preferential adsorption of the reacting ions and/or a good lattice matching between the seed and the crystal. The size of the seeds, which determines the surface area available for crystallization, is not only important for the crystallization kinetics, but also for the solid-liquid separation. Two processes for water softening are known which make use of heterogeneous crystallization. In a pellet reactor [GRA83] $CaCO_3$ is crystallized on a fluidised bed of about 10 m% large sand seeds (0.5-1 mm). The fluidised bed also takes care of the solid-liquid separation, although stationary sand

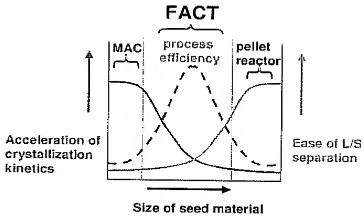

Figure 1
Principle of FACT; the size of the heterogeneous seeds is optimised in order to attain fast crystallization and easy solid-liquid separation in one process.

filters are often applied as polishing filter to remove fines from the softened water. The alternative Membrane Assisted Crystallization (MAC) process uses very small heterogeneous seeds in the order of 1 μm and microfiltration membranes for the recovery of the seeds [VER96]. It was shown that heterogeneous crystallization of $CaCO_3$ on 0.1 m% of small seeds in the MAC-process was significantly faster than the crystallization on 10 m% large seeds in the pellet reactor. The solid-liquid separation by microfiltration was technically feasible, but it will be too expensive for most large-scale processes in which the treated water is the main product of the process - as is the case for water softening. These observations formed the starting point for the development of FACT, which uses intermediate sized heterogeneous seeds typically in the range between 5 and 50 μm. The FACT seeds are larger than the seeds in MAC, but still significantly smaller than in the pellet reactor. The basic idea behind FACT is to maintain the accelerating effect of relatively small seeds observed for MAC and to make solid-liquid separation of the seeds easier/cheaper than in MAC. Figure 1 visualizes the characteristics of MAC, FACT and the pellet reactor.

2. Experimental

Seed selection
The effect of heterogeneous seeds on the crystallization of $CaCO_3$ was measured in batch crystallization experiments. In the tests 0.25 g seeds was added to 225 ml artificial or 250 ml real groundwater. The artificial groundwater was a $NaHCO_3/Na_2CO_3$-solution with a total carbonate concentration of 4.1 mmol/l and a pH of 10.0. Vitens supplied the real groundwater, which had the same composition as in the pilot tests (see table 1). At t=0 supersaturation was created by adding 25 ml of a 25 mM $CaCl_2$-solution to the artificial water or by raising the pH of the real groundwater to 10.0. During the test the change of pH in time is monitored, which is a measure for the $CaCO_3$ crystallization rate. Various seed materials like diatomite, clay, silica, natural chalk and metal oxides/carbonates were tested.

Pilot equipment
A diagram of the FACT pilot unit is presented in figure 2. The pilot consists of a 160 litre MSMPR-crystallizer and a Pulse Tube Filter (PTF)-unit supplied by LFC Lochem, in which tubular filter cloths with a surface area of 0.2 or 0.4 m^2 and a pore size of about 60 μm can be mounted. The pilot unit also contained buffer tanks for the base (a 1 M NaOH solution) and the seed suspension (a 10 m% suspension of a diatomite with d_{50} = 16.3 μm). The typical flow rates of the hard water, the base and the seed suspension are given in figure 2. The applied

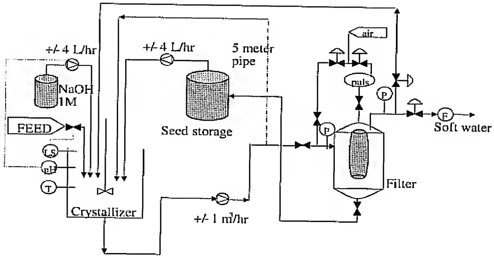

Figure 2
Diagram of the FACT pilot-installation used for the softening of ground- and process water

seed concentration in the crystallizer was 1 g/l. The filter unit is operated batch-wise and a cake is built up on the filter cloth during filtration. When the maximum thickness of 4-5 cm is reached the filter cake is released from the filter cloth by air pulses and the resulting 10 m% seed suspension is recycled to the seed storage tank. The filter can be operated at constant flow (and varying pressure) or constant pressure (and varying flow).
With the FACT pilot plant the softening of two water streams was tested. The first was hard groundwater at a location of Vitens in Goor, which is presently softened by means of a pellet reactor. Softening of groundwater is a typical pre-treatment step in the production of Dutch drinking water. After the FACT test the PTF was replaced by a microfiltration unit containing 4 m^2 membranes with a pore size of 0.45 μm. In this way FACT (with the PTF), MAC (with the membranes) and the actual softening in the pellet reactor could be compared. The second stream tested in the FACT pilot plant was aerated effluent of a biological water treatment of 3 paper mills at Industriewater in Eerbeek. Softening is considered to be an important step to enable closure of the water cycles in the paper mills. The composition of the investigated streams will be presented in table 1 (groundwater, Goor) and table 2 (process water, Eerbeek).

3. Results and discussion

Seed selection
Figure 3 gives an example for the selection of heterogeneous seeds. The feed was the hard groundwater supplied by Vitens. The results for 3 different seeds are shown: chalk with a d_{50} of 1.4 μm, diatomite with a d_{50} of 13.0 μm and calcium silicate with a d_{50} of 16.3 μm.

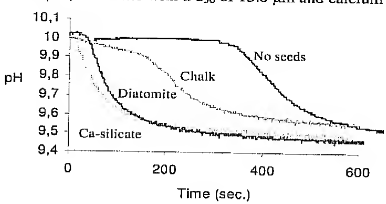

Figure 2
Results seed selection for practical groundwater from Vitens. The faster the decrease of the pH, the faster the precipitation of $CaCO_3$.

The unseeded experiment starts with an induction time, which implies that homogeneous nucleation is slow under the applied conditions. In the seeded experiments the induction time is absent, which implies that the energy barrier for heterogeneous nucleation is smaller and the crystallization faster than for the unseeded reference. Chalk will probably not require heterogeneous nucleation because $CaCO_3$ can grow on the $CaCO_3$ present in this seed. For this reason one would expect a very good interaction between the crystallizing $CaCO_3$ and chalk seed, but remarkably the crystallization of $CaCO_3$ on diatomite and calcium silicate is faster than on chalk. Obviously, the heterogeneous nucleation on diatomite and calcium silicate must be very fast. The large specific surface area of calcium silicate and diatomite, which are respectively 10 and 100 times larger than for chalk, may contribute to the acceleration of the crystallization. There must, however, also be other factors that determine the heterogeneous nucleation rate, because small silica seeds with a specific surface area comparable to that of the calcium silicate did not accelerate the crystallization of $CaCO_3$. Calcium silicate was selected as heterogeneous seed for the FACT pilot plant tests on basis of absence of an induction time and the sharp decrease of the pH in the initial stages of the test.

Table 1 presents the results for the pilot tests for the softening of groundwater with FACT, MAC and the pellet reactor at the drinking water production site of Vitens. The 3 techniques can all reduce calcium in the softened water below the required level of about 40 mg/l. FACT showed the best softening results, but the differences are relatively small. Earlier tests showed that efficient softening in MAC (and FACT) can already be achieved at residence times ≤ 1 min, whereas the residence time in pellet reactors is 3-5 min [VER96]. The reason is the accelerating effect of the small heterogeneous seeds used in MAC and FACT.

The turbidity of the FACT and MAC effluents is below the drinking water specification of 0.4 FTE. Logically, the lowest turbidity is found for the MAC process due to the relatively small pore size of the membranes. The performance of the Pulse Tube Filter (PTF) in the FACT – concept is remarkably good taking in view of the fact that the average seed size (16.3 μm) was much smaller than the pore size of the filter cloth (60 μm). The use of stationary sand filters for the removal of fines from pellet reactor effluent indicates that the turbidity of the pellet reactor effluent is typically higher than 0.4 FTE.

In the pilot tests the filtration with PTF (FACT) and membranes (MAC) are compared. The filtration principle and the pore size of the filter medium are the main differences between the 2 techniques. The PTF uses cake filtration and the filter cloth has a pore size of ± 60 μm. In membrane filtration one tries to avoid the formation of a filter cake on the membrane surface by pumping the suspension with a few m/s through the tubular membranes and the pore size is much smaller, namely 0.45 μm. The filtration of the product suspension with the PTF in the FACT concept was very easy: specific fluxes of 4 $m^3/m^2.hr$ could be reached. Higher fluxes seemed possible, but could not be demonstrated due to the restricted amount of feed.

Table 1 Results for the softening of groundwater with FACT, MAC and the pellet reactor at the drinking water production location of Vitens in Goor (n.m.=not measured).

		Influent	**Effluent FACT**	**Effluent MAC**	**Effluent pellet reactor**
Acidity	pH	7.30	8.6	8.8	8.3
Calcium	mg/l	130	18	22	33
Magnesium	mg/l	15	11	11	11
Hydrogencarbonate	mg/l	375	236	240	279
Carbonate	mg/l	0	6	11	n.m.
Turbidity	FTE	n.m.	0.16	<0.05	n.m.

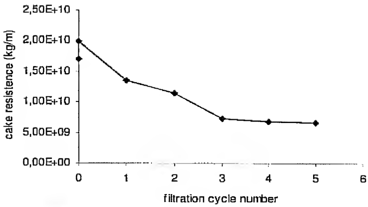

Figure 4

Development of the filter cake resistance for 5 consecutive filtration cycles with the PTF in the FACT pilot plant

In a filtration cycle of 4 hours the pressure over the PTF increased from 0.2 bar to 1.3 bar due to the increasing thickness of the filter cake. The pressure increases linearly with a gradient of 0.5 bar/hr during the first 1.5 hrs of a filtration cycle, but it levels off to 0.15 bar/hr at the end of the cycle. This can be explained by the tubular shape of the filter, which causes a non-linear increase of the thickness of the filter cake in time. The measured filtration data and Darcy's law for incompressible filter cakes were used to calculate the filter cake resistance. Figure 4 shows the development of the filter cake resistance during 5 consecutive filtration cycles with the PTF. The observed decrease of the resistance is consistent with the increase of the particle size due to the growth of the seeds with $CaCO_3$ in the FACT-process. This observation also indicates that fouling of the filter, which would increase the resistance, does not seem to occur. Longer tests are needed to confirm this preliminary conclusion. The estimated total costs for the softening of drinking water by means of FACT amount € 0.12/m^3, which is lower than the reference costs of € 0.17/m^3 for pellet reactor softening.
The specific flux of the membranes was 0.4 m^3/m^2.bar.hr, which is about 10 times lower than for the PTF. So, the pilot tests re-confirmed that solid-liquid separation of small seeds by membranes in MAC is technically feasible, but expensive due to the relatively low flux of the softened water through the membranes and the costs of the membranes.

Process water softening
Process water originating from the combined biological water treatment of 3 paper mills has been softened with FACT. Table 2 gives the composition of the feed and the softened water. Both the Ca- and the HCO_3-content are much higher than for the groundwater. The NaOH consumption is higher than for groundwater due to the buffering capacity of the HCO_3^-. The Ca-level is reduced by 80%, which is sufficient to meet the specification for recycling of the water. The specific filtration flux for the PTF for the softened process water was in the order of 2.5 m^3/m^2.hr at pressures between 0.5 and 2.5 bar. The filter cake resistance was 2.10^{10} kg/m, which is higher than the value found for the softening of groundwater (see figure 4).

Table 2 Results for the softening of process water with FACT at Industriewater in Eerbeek.

		Influent	**Effluent**
Acidity	PH	8.1	8.22
Ca	mg/l	352	73
Mg	mg/l	15	9.4
Hydrogen carbonate	Mmol/	17.4	9.4
Dried solids content	mg/l	3	1

The main reason is the presence of fine solids in the feed, which makes the filtration more difficult. During the pilot tests with the process water filtration at constant pressure (instead of constant flow) has been tried. At a constant pressure of ± 3.75 bar the initial flux was 13 m^3/m^2.hr, which gradually decreases to 4 m^3/m^2.hr. The total amount of filtrate was ± 7.5 m^3/m^2 for the first hour. The positive effect of the higher pressure is a significant increase of the specific flux. The drawbacks of this method are the fluctuating flow, which implies that buffer tanks will be needed in processes requiring a constant feed and/or product flow and the increased operating costs for maintaining the higher pressure.

4. Conclusions

Filtration Assisted Crystallization Technology (FACT) is a hybrid process, based on the use of heterogeneous seeds between 5 and 50 μm with the aim to realise a fast crystallization and an easy solid-liquid separation. The concept is generic and can for instance be applied for the removal of Ca^{2+}, F^- or PO_4^{3-} from process- or wastewater. A further promising application of FACT is to use the concept for a controlled change of the shape and/or size of solid products.
Batch experiments proved that heterogeneous seeds like diatomite (d_{50}=13.0 μm) and calcium silicate (d_{50}=16.3 μm) significantly accelerate the crystallization of $CaCO_3$. Surprisingly, these seeds with were even more effective than chalk seeds (d_{50}=1.4 μm), which predominantly consist of $CaCO_3$.
Pilot plant experiments have been carried out for the FACT concept at a scale of 1 m^3/hour using calcium silicate as heterogeneous seed and a Pulse Tube Filter for the solid-liquid separation. Two industrial ground- and process water streams were softened successfully with FACT: the Ca^{2+}-concentrations could be decreased by 80-85%, the solids content in the filtrate was below specification and high filtration fluxes between 2.5 and 4 m^3/m^2.hr could be realised with the Pulse Tube Filter at relatively low pressures between 0.2 and 2.5 bar. The specific flux with the Pulse Tube Filter in FACT was 10 times higher than the flux for microfiltration membranes (MAC).
The experimentally measured crystallization and filtration data were used in a rough economic evaluation of the costs for the softening of groundwater with FACT. This evaluation showed that FACT could be about 30% cheaper than the costs for softening with the pellet reactor, the state-of-the-art technique for the production of Dutch drinking water.

5. References

[GRA83] Graveland, J.C. van Dijk, P.J. de Moel, J.H.C.M. Oomen; Developments in water softening by means of pellet reactors; Journal AWWA, 75 (1983) nr. 12, p.619-625.

[VER96] Verdoes, D. and Hanemaaijer, J.H., Proceedings of the Bremen International Workshop on Industrial Crystallization (Eds. J. Ulrich and K. Wangnick), Bremen (FRG), 12-13 September 1996, p. 92-99.

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